Alteration of shape and field narrowing of the absorption line of light alkali-metal atoms in an atmosphere of heavy inert gases

F. Kh. Gel'mukhanov and A. I. Parkhomenko

Institute of Automation and Electrometry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia

(Submitted 20 January 1995)
Zh. Éksp. Teor. Fiz. **107**, 1853–1867 (June 1995)

We predict an alteration of shape and a narrowing of the absorption line of light alkali-metal atoms (^{7}Li and ^{23}Na) in an atmosphere of heavy inert gases (Xe and Kr) as the radiation intensity increases. The halfwidth of the line at halfheight may decrease by a factor of 1.3 to 1.5. The upper part of the narrowed line profile is practically triangular. The critical radiation intensity I_0 at which lineshape narrowing begins depends on the buffer gas pressure (the dependence is linear at pressures much lower than 1 torr and quadratic at pressures much higher than 1 torr). At a pressure of about 1 torr the critical intensity I_0 is of order 10^{-3} W/cm^{-2}. The effect is caused by optical pumping to the ground-state hyperfine components and by a strong difference (by a factor of M_B/M) in the collisional relaxation rates in the orientations and magnitude of the velocity **v** of the resonant particles under the condition $M \ll M_B$, where M and M_B are the masses of the resonant and buffer particles, respectively. © *1995 American Institute of Physics.*

1. INTRODUCTION

Among the most important characteristics in the nonlinear spectroscopy of atoms and molecules are the absorption lineshape and linewidth of the object studied. It is well known[1,2] that increasing the intensity of the radiation leads to a broadening of the absorption line owing to saturation effects. In this paper we focus on the possibility of a markedly different situation: narrowing of the absorption line when the radiation intensity increases. Using as an example three-level particles with a Λ-configuration of the levels, which model light alkali-metal atoms (^{7}Li and ^{23} Na), we show that in an atmosphere of heavy buffer particles ($M/M_B \ll 1$, where M and M_B are the masses of the resonant and buffer particles respectively), increasing the radiation intensity leads to deformation and narrowing of the absorption line profile.

2. THE ABSORPTION LINESHAPE IN THE HYPERFINE SPLITTING OF THE GROUND STATE

Let us examine the interaction of a traveling monochromatic wave and absorbing particles mixed with buffer particles. The level diagram of the absorbing particles is depicted in Fig. 1. Here the levels n and l are the components of the hyperfine structure of the ground state, with no restrictions imposed on level separation. The level m corresponds to the excited state, and g_i is the statistical weight of the ith level ($i=n,l,m$). We ignore collisions between the absorbing particles, assuming the density N_B of the buffer gas to be much higher than the density N of the absorbing gas ($N_B \gg N$).

This level diagram gives a good picture of the real structure of the ground and first excited states of light alkali-metal atoms (^{7}Li and ^{23}Na). Indeed, the ground level of these atoms is split into two hyperfine components. The component separation is comparable with the Doppler width and so the ground state is modeled by two levels, n and l (for ^{6}Li atoms the hyperfine-component separation in the ground state is much smaller than the Doppler width, and one level is therefore sufficient for modeling the ground state of ^{6}Li atoms). For ^{7}Li and ^{23}Na atoms (nuclear spin 3/2) the level n is characterized by a statistical weight $g_n=3$ (total atomic angular momentum $F=1$) and the level l by a statistical weight $g_l=5$ ($F=2$).

The level m models a group of levels that are the components of the hyperfine structure of the exited states $P_{1/2}$ and $P_{3/2}$. Such modeling of a group of levels by a single level is possible because for ^{7}Li and ^{23}Na atoms the hyperfine splitting of these excited states is small compared to the Doppler absorption linewidth. Radiation involves only one fine component of an excited state, $P_{1/2}$ or $P_{3/2}$.

For ^{7}Li and ^{23}Na atoms the limiting case of strong collisional coupling between the fine components $P_{1/2}$ and $P_{3/2}$ is realized (the Massey parameter is much smaller than unity). Hence from the collision viewpoint a pair of fine components is interpreted as a single level with an elevated statistical weight. If during the lifetime of the excited state collisions have a low probability of occurring, $g_m=8$ in the excitation of the D_1-line (radiation involves the fine level $P_{1/2}$ with two hyperfine components, $F=1$ and $F=2$) and $g_m=16$ in the excitation of the D_2-line (radiation involves the fine level $P_{3/2}$ with four hyperfine components, $F=0$, $F=1$, $F=2$, and $F=3$). But if the number of collisions with the buffer particles during the lifetime of the excited state is large, in modeling ^{7}Li and ^{23}Na atoms by a three-level scheme we must put $g_m=24$ in the excitation of both the D_1-line and the D_2-line.

The interaction of particles with radiation in steady-state and spatially homogeneous conditions is described by the following equations for the density matrix:[1]

$$\Gamma_m \rho_m(\mathbf{v}) = S_m(\mathbf{v}) + N[P_l(\mathbf{v}) + P_n(\mathbf{v})],$$

$$S_i(\mathbf{v}) + \Gamma_{mi}\rho_m(\mathbf{v}) = NP_i(\mathbf{v}), \qquad (2.1)$$

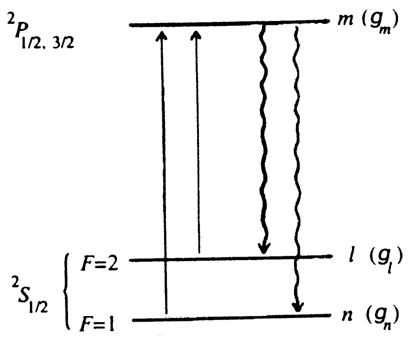

FIG. 1. The energy level diagram. The straight arrows stand for transitions induced by radiation, and the wavy arrows designate spontaneous radiative transitions.

$$\left[\frac{\Gamma_m}{2}-i(\Omega_{0i}-\mathbf{kv})\right]\rho_{mi}(\mathbf{v})=S_{mi}(\mathbf{v})+iG\left[\rho_i(\mathbf{v})-\frac{g_i}{g_m}\rho_m(\mathbf{v})\right],$$

where

$$NP_i(\mathbf{v})=-2\mathrm{Re}[iG^*\rho_{mi}(\mathbf{v})],\quad |G|^2=\frac{BI}{2\pi},$$

$$B=\frac{\lambda^2\Gamma_m w_m}{4\hbar\omega},\quad w_m=\frac{g_m}{g_l+g_n},\tag{2.2}$$

$$\Gamma_m=\Gamma_{mn}+\Gamma_{ml},\quad \Omega_{0i}=\omega-\omega_{mi}\quad (i=n,l).$$

Here $\rho_i(\mathbf{v})$ specifies the velocity distribution of the particles on the level i; $N=\rho_n+\rho_l+\rho_m$ is the absorbing-particle concentration ($\rho_i=\int\rho_i(\mathbf{v}\,d\mathbf{v})$; Γ_{mi} is the rate of spontaneous relaxation of the level m in the channel $m\rightarrow i$; ω, λ, and $\mathbf{k}$ are the frequency, wavelength and wave vector of the radiation; ω_{mi} is the $m-i$ transition frequency; $S_m(\mathbf{v})$, $S_i(\mathbf{v})$, and $S_{mi}(\mathbf{v})$ are the collision integrals; and $I=cE^2/8\pi$ is the absolute value of the Poynting vector, which characterizes the radiation energy flux. In writing the expression for the Einstein coefficient B in (2.2) we allowed for the fact that the ratio of the rates of radiative transitions from the level m to the hyperfine components n and l is determined by the ratio of statistical weights:[3]

$$\frac{\Gamma_{mn}}{\Gamma_{ml}}=\frac{g_n}{g_l}.\tag{2.3}$$

The probability $P_i(\mathbf{v})$ of radiation being absorbed per unit time in the $m-i$ transition by a particle with a fixed velocity $\mathbf{v}$ is determined by the off-diagonal element $\rho_{mi}(\mathbf{v})$ of the density matrix (the coherence). Note that the last equation in (2.1) for the off-diagonal element $\rho_{mi}(\mathbf{v})$ is valid only if we ignore the coherence $\rho_{ln}(\mathbf{v})$ between the hyperfine components n and l. This approximation is true if the radiation intensities are not too high:[4]

$$|G|^2\ll\Gamma\omega_{ln},\tag{2.4}$$

where Γ is the homogeneous halfwidth of the absorption line, and ω_{ln} is the $l-n$ transition frequency.

When the collisions have no phase memory (an assumption common in nonlinear atomic spectroscopy), the off-diagonal collision integral has the form

$$S_{mi}(\mathbf{v})=-(\nu_{mi}+i\Delta_{mi})\rho_{mi}(\mathbf{v}),\quad (i=n,l),\tag{2.5}$$

where ν_{mi} and Δ_{mi} are the impact broadening and collisional shift of the levels, respectively. Combining (2.1) and (2.2) with (2.5) yields

$$NP_i(\mathbf{v})=\frac{BI}{\pi\Gamma_j}Y_i(\mathbf{v})\left[\rho_i(\mathbf{v})-\frac{g_i}{g_m}\rho_m(\mathbf{v})\right],\tag{2.6}$$

where

$$Y_i(\mathbf{v})=\frac{\Gamma_j^2}{\Gamma_j^2+(\Omega_i-\mathbf{kv})^2},\quad \Omega_i=\Omega_{0i}-\Delta_{mi},$$

$$\Gamma_1=\frac{\Gamma_m}{2}+\nu_{mn},\quad \Gamma_2=\frac{\Gamma_m}{2}+\nu_{ml},\tag{2.7}$$

$$i=n,\quad j=1;\quad i=l,\quad j=2.$$

Here Γ_1 and Γ_2 are the homogeneous halfwidths of the absorption lines for the $m-n$ and $m-l$ transitions, respectively.

For alkali-metal atoms in an atmosphere of inert gases the cross sections of the collisional $n-l$ and $l-n$ transitions between the hyperfine components are many orders of magnitude smaller than the gas-kinetic cross sections.[5] Bearing this in mind, below we examine the case in which there is no collisional exchange between the hyperfine components n and l.

We integrate the second equation in (2.1) with respect to $\mathbf{v}$ and allow for the fact that in elastic collisions

$$\int S_i(\mathbf{v})d\mathbf{v}=0.\tag{2.8}$$

As a result we get

$$\Gamma_{mi}\rho_m=NP_i\quad P_i=\int P_i(\mathbf{v})d\mathbf{v},\tag{2.9}$$

which yields (see also Ref. 6)

$$\frac{P_n}{P_l}=\frac{\Gamma_{mn}}{\Gamma_{ml}}=\frac{g_n}{g_l}.\tag{2.10}$$

We see that the ratio of the total probabilities of radiation absorption for the $m-n$ and $m-l$ transitions depends on neither radiation intensity nor radiation frequency. It characterizes the process of optical pumping of the hyperfine components of the ground state and is a consequence of the absence of collisional exchange between the hyperfine components n and l (see Ref. 6).

To find the absorption lineshape we limit ourselves to weak fields by assuming that the induced transition rate is low compared to the rate Γ_m of the radiative decay of the excited level m and the rates of collisional relaxation of nonequilibrium structures in the populations $\rho_i(\mathbf{v})$. In the case of heavy buffer particles, the condition $M\ll M_B$ makes it possible to distinguish two scales of the collisional relaxation rate: in orientations (ν_i) and in the magnitude ($\nu_i M/M_B$) of the velocity $\mathbf{v}$ of the resonant particles. Here ν_i is the effective transport frequency of elastic collisions of a particle on the level i with the buffer gas. The frequency ν_i is related to the coefficient D_i of diffusion of particles in the state i as follows:

$$\nu_i=\frac{\bar{v}^2}{2D_i}, \quad \bar{v}^2=\frac{2k_BT}{M}, \tag{2.11}$$

where k_B is the Boltzmann constant, and T is the temperature. But if the buffer particles are not heavy ($M\gtrsim M_B$), the rates of collisional relaxation in orientations (ν_i) and in the magnitude of $\mathbf{v}$ are approximately the same. Thus, the weak-field condition can be written as

$$\begin{aligned} &P_i\ll\Gamma_m, \ \min\left\{y\nu_i, \, y\nu_i\frac{M}{M_B}\right\}, \quad y\ll 1, \\ &P_i\ll\Gamma_m, \ \min\left\{\nu_i, \, \nu_i\frac{M}{M_B}\right\}, \quad y\gtrsim 1, \end{aligned} \tag{2.12}$$

where $y=\Gamma/k\bar{v}$, and $\Gamma\equiv\Gamma_1\approx\Gamma_2$. In the Doppler limit ($y\ll 1$), the weak-field condition (2.12) contains y as a factor. The reason is that radiation will be absorbed only by atoms whose velocity projections v_z on the direction of the wave vector $\mathbf{k}$ find themselves, owing to collisions, in a Bennett hole of width $\Delta v_z=\Gamma/k=y\bar{v}$.

The condition (2.12) means that the fraction of atoms in the excited state is small ($\rho_m\ll N$) and that the levelpopulations $i=n,l$ have a velocity distribution closely resembling the Maxwellian:

$$\rho_i(\mathbf{v})=\rho_iW(v), \quad W(v)=(\sqrt{\pi}\bar{v})^{-3}\exp\left(-\frac{\mathbf{v}^2}{\bar{v}^2}\right), \quad i=n,l. \tag{2.13}$$

In these conditions Eq. (2.6) for $P_i(\mathbf{v})$ has the form (here and in what follows we assume that the homogeneous halfwidths of the absorption lines, Γ_1 and Γ_2, for the $m-n$ and $m-l$ transitions are equal: $\Gamma_1=\Gamma_2\equiv\Gamma$):

$$P_i(\mathbf{v})=\frac{BI}{\pi\Gamma}\frac{\rho_i}{N}Y_i(\mathbf{v})W(v). \tag{2.14}$$

Employing the normalization condition $\rho_n+\rho_l\simeq N$ (we have allowed for the fact that $\rho_m\ll N$) and assuming that the homogeneous halfwidth Γ and the collisional shift Δ_{mi} are independent of v, we find from (2.10), (2.13), and (2.14) the following expressions for the population $\rho_i(\mathbf{v})$ and the total integral absorption probability P:

$$\begin{aligned} &\rho_n(\mathbf{v})=\frac{Nw_nW(v)f(x_l)}{w_nf(x_l)+w_lf(x_n)}, \\ &\rho_l(\mathbf{v})=\frac{Nw_lW(v)f(x_n)}{w_nf(x_l)+w_lf(x_n)}, \end{aligned} \tag{2.15}$$

$$P\equiv P_n+P_l=\sqrt{\pi}\,\kappa\Gamma_m\frac{f(x_n)d(x_l)}{w_nf(x_l)+w_lf(x_n)}, \tag{2.16}$$

where

$$\kappa=\frac{2|G|^2}{\Gamma_mk\bar{v}}, \quad w_i=\frac{g_i}{g_n+g_l}, \quad f(x_i)\equiv\mathrm{Re}[w(z_i)],$$

$$w(z_i)=\exp\{-z_i^2\}\left(1+\frac{2i}{\sqrt{\pi}}\int_0^{z_i}\exp t^2\,dt\right), \tag{2.17}$$

$$z_i=x_i+iy, \quad x_i=\frac{\Omega_i}{k\bar{v}}, \quad y=\frac{\Gamma}{k\bar{v}}, \quad i=n,l.$$

The probability integral with a complex-valued argument, $w(z)$, has been tabulated in Ref. 7. Equation (2.16) describes the lineshape of absorption of a weak field by alkali-metal atoms in an atmosphere of inert buffer gases. When the hyperfine components n and l formally merge (the limit $\omega_{ln}\to 0$), Eq. (2.16) for P becomes, as it should, the formula for a two-level system with level degeneracy.

3. THE CASE OF DOPPLER BROADENING

In the limit of large Doppler broadening,

$$y\ll 1, \tag{3.1}$$

we have the following expressions for the function $f(x)$ specified in (2.17):

$$\begin{aligned} &f(x)=\exp\{-x^2\}, \quad |x|\lesssim 1, \\ &f(x)=\exp\{-x^2\}+\frac{y}{\sqrt{\pi}\,x^2}, \quad |x|\gg 1. \end{aligned} \tag{3.2}$$

If y is so small that

$$y\ll\sqrt{\pi}\,x^2\exp\{-x^2\} \tag{3.3}$$

even for $|x|\gg 1$, the first equation in (3.2) also holds for $f(x)$. Here the absorption probability P specified by (2.16) can be written as

$$\begin{aligned} &P=\sqrt{\pi}\,\kappa\Gamma_m\phi, \quad \phi=\frac{\exp\{-\delta^2/4-x_0^2\}}{w_l\exp\{\delta x_0\}+w_n\exp\{-\delta x_0\}}, \\ &\delta=\frac{\omega_{ln}}{k\bar{v}}, \quad x_0=\frac{\omega-\omega_0}{k\bar{v}}, \quad \omega_0=\frac{\omega_{mn}+\omega_{ml}}{2}, \end{aligned} \tag{3.4}$$

where δ is the dimensionless separation of the hyperfine structure components, and x_0 is the dimensionless detuning of the radiation frequency from the arithmetic-mean frequency ω_0 of the $m-n$ and $m-l$ transitions. The absorption probability P as a function of x_0 is asymmetric if $w_n\neq w_l$.

The peak (the center of the line) in the absorption P specified by (3.4) is reached at the point

$$x_{0\max}\approx\frac{\delta(w_n-w_l)}{2} \tag{3.5}$$

and is displaced in relation to the arithmetic-mean frequency ω_0 toward the hyperfine component with the greater statistical weight. For ^{7}Li and ^{23}Na atoms the factor w_l-w_n is equal to 0.25, and the displacement of the absorption-line center from the arithmetic-mean frequency ω_0 amounts to $\omega_{ln}/8$.

4. THE LINESHAPE IN A LORENTZ GAS

Let us now find the probability of absorption of a weak field using the kinetic equations (2.1) for the density matrix in the limit of a heavy buffer gas, $M/M_B \ll 1$ (a Lorentz gas[8]). For a Lorentz gas the diagonal collision integrals have the form[8,9]

$$S_i(\mathbf{v}) = -\frac{1}{v^2}\frac{\partial}{\partial v}[v^2 s_i(\mathbf{v})] + N_B v \int d\mathbf{n}\sigma_i(v,\vartheta)[\rho_i(\mathbf{v}') - \rho_i(\mathbf{v})], \tag{4.1}$$

where

$$s_i(\mathbf{v}) = -\frac{M}{M_B}\nu_i(v)v\left[1+\bar{v}^2\frac{\partial}{\partial v^2}\right]\rho_i(\mathbf{v}),$$
$$\nu_i(v) = N_B v \sigma_i(v), \tag{4.2}$$
$$\sigma_i(v) = 2\pi\int_0^\pi \sigma_i(v,\vartheta)(1-\cos\vartheta)\sin\vartheta\, d\vartheta,$$

$$\cos\vartheta = \mathbf{nn}', \quad \mathbf{n} = \frac{\mathbf{v}}{v}, \quad \mathbf{n}' = \frac{\mathbf{v}'}{v}, \quad v' = v = |\mathbf{v}|, \quad i = n,l,m.$$

Here $\mathbf{v}$ and $\mathbf{v}'$ are the velocities of an absorbing particle before and after the collision; $\sigma_i(v,\vartheta)$ is the cross section of elastic ($v'=v$) scattering of an absorbing particle in the state i through the angle ϑ; and $\sigma_i(v)$ and $\nu_i(v)$ are the transport cross section and collision frequency. For a Lorentz gas the transport frequency $\nu_i(v)$ (we can assume that $\nu_i(v)$ is approximately equal to ν_i, with ν_i defined in (2.11)) is responsible for the collisions that change the direction of the velocity but not the magnitude. A noticeable change in the absolute value of the velocity of the light absorbing particles occurs in $M_B/M \gg 1$ collisions, while the direction of the velocity changes in a single collision. The term in the right-hand side of (4.1) with the derivative describes the change of the absolute value of the velocity of the absorbing particles in collisions. The integral term in (4.1) is the collision integral with respect to the change in the direction $\mathbf{n}$ of the velocity.

We substitute the collision integral (4.1) into the second equation in (2.1) and integrate over the orientations of the velocity vector $\mathbf{v}$, i.e., with respect to $d\mathbf{n}/4\pi$. The result is

$$\Gamma_{mi}\rho_m(v) = NP_i(v) - \frac{M}{M_B}\frac{1}{v^2}\frac{\partial}{\partial v}\left[v^3\nu_i(v)\left(1 + \bar{v}^2\frac{\partial}{\partial v^2}\right)\rho_i(v)\right], \tag{4.3}$$

where

$$\rho_j(v) = \int \rho_j(\mathbf{v})\frac{d\mathbf{n}}{4\pi}, \quad P_i(v) = \int P_i(\mathbf{v})\frac{d\mathbf{n}}{4\pi},$$
$$i = n,l, \quad j = n,l,m. \tag{4.4}$$

In the limit of low radiation intensities $P_i \to 0$ (more precisely, if the conditions in (2.12) are met) we can put $\rho_m(v)=0$ and $P_i(v)=0$ in (4.3). The vanishing of the term with the derivatives implies $\rho_i(v) = \rho_i W(v)$, so that we arrive at the previous expressions (2.14) and (2.16) for the absorption probability.

The situation changes dramatically, however, as the radiation intensity grows, when the conditions in (2.12) are already violated but

$$y\nu_i\frac{M}{M_B} \ll P_i \ll \Gamma_m,\ y\nu_i, \quad y \ll 1,$$
$$\nu_i\frac{M}{M_B} \ll P_i \ll \Gamma_m,\ \nu_i, \quad y \gtrsim 1. \tag{4.5}$$

Only a Lorentz gas ($M \ll M_B$) meets such conditions. What these conditions mean is that the stimulated transition rate is sufficiently large for isotropic nonequilibrium structures to emerge in the population distributions in the absolute value of velocity, v, on levels n and l (the collisional relaxation rate for such structures is $\nu_i M/M_B$). At the same time the stimulated transition rate is not sufficiently high for anisotropic Bennett structures to appear on the levels n and l (their collisional relaxation rate is ν_i).

If conditions (4.5) are met, the term on the right-hand side of Eq. (4.3) with the derivatives can be neglected (this becomes clear after direct substitution of the solutions (4.9) and (4.14) into (4.3) is done), and Eq. (4.3) assumes the form

$$\Gamma_{mi}\rho_m(v) = NP_i(v). \tag{4.6}$$

This yields

$$\frac{P_n(v)}{P_l(v)} = \frac{\Gamma_{mn}}{\Gamma_{ml}}. \tag{4.7}$$

In contrast to (2.10), which follows from an exact property of the collision integral (2.8), Eq. (4.7) is a consequence of an approximate property of the collision integral for a Lorentz gas: $\int S_i(\mathbf{v})\, d\mathbf{n} \approx 0$.

Let us find the absorption probability $P_i(v)$ when the conditions (4.5) are met. Since these conditions impose a restriction on the radiation intensity, we can neglect the population $\rho_m(\mathbf{v})$ in Eq. (2.6) for $P_i(\mathbf{v})$ and also assume that the amplitude of the anisotropic part of the distribution $\rho_i(\mathbf{v})$ on the level $i=n,l$ is small compared to the amplitude of the isotropic part. Then

$$NP_i(\mathbf{v}) = \frac{BI}{\pi\Gamma_j}Y_i(\mathbf{v})\rho_i(v), \tag{4.8}$$

where $\rho_i(v)$ is the isotropic part of the distribution $\rho_i(\mathbf{v})$. Here, as in (2.14), we have assumed that the homogeneous halfwidths of the absorption lines involving the $m-n$ and $m-l$ transitions are equal: $\Gamma_1 = \Gamma_2 \equiv \Gamma$. Integrating (4.8) over the orientations of $\mathbf{v}$, we find the probability of radiation absorption per unit time (the absorption rate) involving the $m-i$ transition by a particle with a fixed absolute value v of velocity:

$$NP_i(v) = \frac{\kappa\Gamma_m}{2}\frac{\Psi_i(t)}{t}\rho_i(t), \tag{4.9}$$

where

$$\Psi_i(t) = \tan^{-1}\left(\frac{t+x_i}{y}\right) + \tan^{-1}\left(\frac{t-x_i}{y}\right), \tag{4.10}$$

with $t = v/\bar{v}$, and $i=n,l$. The quantities κ, y, and x_i were defined in (2.17).

To find the populations $\rho_i(v)$ in (4.9), we must sum the first three equations in (2.1) and integrate over the orientations of $\mathbf{v}$ with the help of the collision integral (4.1). This leads to the following equation:

$$\sum_{i=n,l,m} \nu_i(v)\left(1+\bar{v}^2 \frac{\partial}{\partial v^2}\right)\rho_i(v)=0. \qquad (4.11)$$

Ignoring $\rho_m(v)$ in (4.11), allowing for the conditions (4.5), and combining (4.11) with (4.7) and (4.9) yields the following expression for the total population with respect to the absolute value of velocity:

$$N(v)\approx\rho_n(v)+\rho_l(v)=\frac{Nq(t)}{4\pi\bar{v}^3\int_0^\infty t^2q(t)\,dt}, \qquad (4.12)$$

where

$$q(t)=[1+\alpha(t)]\exp\left[-t^2-\int^t \frac{d\alpha(t)/dt}{\alpha(t)+\beta(t)}\,dt\right],$$
$$\alpha(t)=\frac{g_l}{g_n}\frac{\Psi_n(t)}{\Psi_l(t)},\quad \beta(t)=\frac{\nu_n(v)}{\nu_l(v)}. \qquad (4.13)$$

Clearly, the total population $N(v)$ differs from the Maxwellian when $\nu_n(v)\neq\nu_l(v)$. For hyperfine components, however, it can be assumed with high accuracy that the transport frequencies are equal: $\nu_n(v)=\nu_l(v)$. Then (4.12) yields $N(v)=NW(v)$, and we arrive at the following simple form of the expression for the populations $\rho_i(v)$:

$$\rho_n(v)=\frac{Nw_nW(v)\Psi_l(t)}{w_n\Psi_l(t)+w_l\Psi_n(t)},$$
$$\rho_l(v)=\frac{Nw_lW(v)\Psi_n(t)}{w_n\Psi_l(t)+w_l\Psi_n(t)}. \qquad (4.14)$$

For the total integral probability of radiation absorption by a Lorentz gas,

$$P_L=4\pi\int_0^\infty v^2[P_n(v)+P_l(v)]\,dv, \qquad (4.15)$$

we obtain, via (4.9) and (4.14), the following expression:

$$P_L=\frac{2\kappa\Gamma_m}{\sqrt{\pi}}\int_0^\infty \frac{t\exp\{-t^2\}\Psi_n(t)\Psi_l(t)}{w_n\Psi_l(t)+w_l\Psi_n(t)}\,dt. \qquad (4.16)$$

For two-level particles ($\omega_{ln}\to 0$) Eqs. (4.16) and (2.16) give the same result: $P=P_L=\sqrt{\pi}\,\kappa\Gamma_m f(x)$.

In the Doppler limit (3.1) the absorption probability P_L specified by (4.16) can be written as

$$P_L=\sqrt{\pi}\,\kappa\Gamma_m\phi_L,\quad \phi_L=\exp\left[-\left(\frac{\delta}{2}+|x_0|\right)^2\right], \qquad (4.17)$$

where x_0 and δ have been defined in (3.4). In contrast to the absorption probability P specified by (3.4), the absorption probability P_L specified by (4.17) is a symmetric function of the detuning x_0 of the radiation frequency from the arithmetic-mean frequency ω_0 of the $m-n$ and $m-l$ transitions.

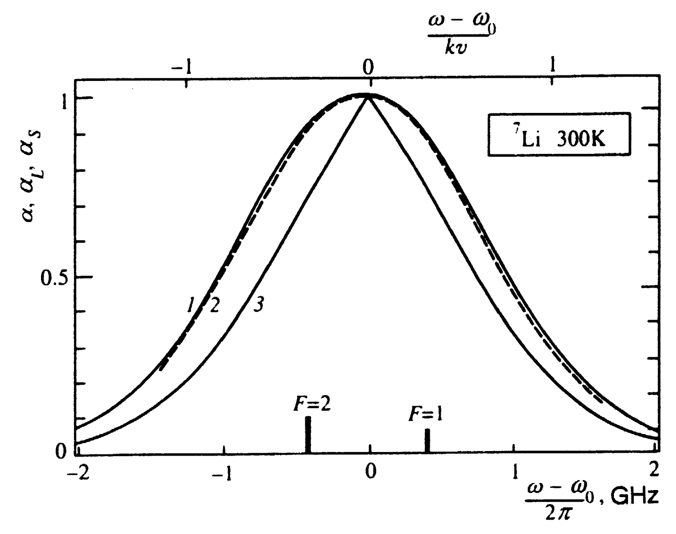

FIG. 2. The absorption lineshapes for ^{7}Li atoms in the Doppler limit $y\ll 1$ at $T=300$ K ($\omega_{ln}=5.049\times 10^9\ s^{-1}$ (Ref. 10) and $\delta=0.636$). The vertical solid short lines $F=1$ and $F=2$ mark the frequencies in resonance with the $m-n$ and $m-l$ transitions. Curve *1* corresponds to a low radiation intensity (conditions (2.12), calculation by Eq. (3.4)); curve *2* corresponds to an elevated radiation intensity and the strong-collision model (conditions (5.5), calculation by Eq. (5.6)); and curve *3* corresponds to an elevated radiation intensity and a Lorentz gas (conditions (4.5), calculation by Eq. (4.17)).

5. DISCUSSION

Radiation absorption described by Eqs. (2.16) and (4.16) is characterized by the lineshapes

$$\alpha=\frac{P}{P_{\max}},\quad \alpha_L=\frac{P_L}{(P_L)_{\max}}, \qquad (5.1)$$

where "max" denotes the maximum of the function. For Doppler broadening, with the aid of (3.4) and (4.17) we find that

$$\frac{\alpha_L}{\alpha}=\exp\{-\delta|x_0|\}(w_l\exp\{\delta x_0\}+w_n\exp\{-\delta x_0\})\,\frac{\phi_{\max}}{(\phi_L)_{\max}}. \qquad (5.2)$$

Noting that in cases interesting from the practical viewpoint (we have in mind ^{7}Li and ^{23}Na atoms, for which $w_n=3/8$, $w_l=5/8$, and $\delta\sim 1$) the ratio $\phi_{\max}/(\phi_L)_{\max}$ is close to unity, we conclude from (5.2) that $\alpha_L<\alpha$. This means that the profile of the lineshape α_L is narrower than that of α. In other words, in a Lorentz gas the absorption line for three-level particles narrows as the radiation intensity increases [i.e., as the conditions (2.12) are replaced by (4.5)]

The curves *1* and *3* in Figs. 2 and 3 illustrate the alteration of shape and the narrowing of the absorption line for ^{7}Li and ^{23}Na atoms in heavy inert buffer gases. The most suitable inert buffer gas from the viewpoint of registering the effect is xenon. For the ^{7}Li–Xe system with a natural xenon-isotope content the mass ratio M_B/M is 18.9, and for the ^{23}Na–Xe system $M_B/M=5.7$, so that the condition for describing a system by a Lorentz gas, $M_B/M\gg 1$, is satisfied fairly well. As Figs. 2 and 3 show, the linewidth at halfheight becomes smaller, as the radiation intensity increases, by a factor of 1.33 for ^{7}Li atoms at $T=300$ K and by a factor of

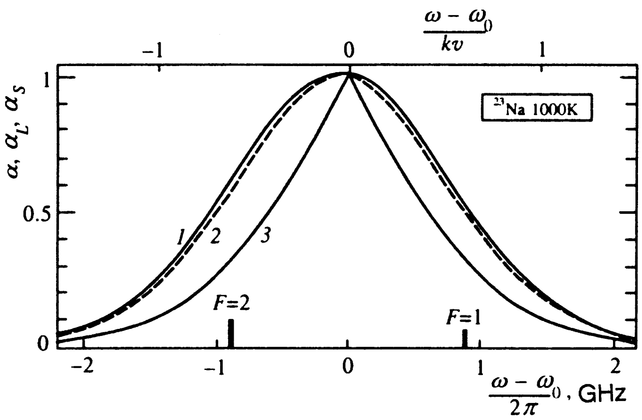

FIG. 3. The absorption lineshapes for ^{23}Na atoms in the Doppler limit $y \ll 1$ at $T=1000$ K ($\omega_{ln}=1.113\times 10^{10}$ s^{-1} (Ref. 10) and $\delta=1.227$). The curves *1*, *2*, and *3* correspond to the same situations as in Fig. 2.

1.50 for ^{23}Na atoms at $T=1000$ K. The upper part of the narrowed line profile (curves *3* in Figs. 2 and 3) is practically triangular (the left and right derivatives of α_L at the point $x_0=0$ do not coincide).

The narrowing effect is manifested most vividly in the Doppler limit $y \ll 1$ and when the dimensionless separation δ of the hyperfine components is of order unity. Since δ is temperature-dependent, so is the size of the effect. For ^{7}Li atoms the narrowing effect is stronger at low temperatures ($T \lesssim 300$ K), while for ^{23}Na atoms this effect is stronger at elevated temperatures ($T \sim 1000$ K).

In the limit

$$|z_i| \equiv \sqrt{x_i^2+y^2} \gg 1, \quad (i=n,l), \tag{5.3}$$

which is true in the case of homogeneous broadening, $y \gg 1$, or when the dimensionless detuning of the radiation frequency is large, $|x_i| \gg 1$ (absorption in the wings of the line or in practically the entire absorption line when the separation of the hyperfine components is large, $\delta \gg 1$), the absorption probabilities P specified by (2.16) and P_L specified by (4.16) are given by the same expression:

$$P=P_L=\frac{\kappa y \Gamma_m}{y^2+\delta^2/4+x_0^2+(w_l-w_n)\delta x_0}. \tag{5.4}$$

Thus, in the case of homogeneous broadening ($y \gg 1$) there is no narrowing effect.

The upper bound on the radiation intensity in (4.5) is not important for the existence of the effect of narrowing of the absorption line and is introduced here solely to simplify solution of the problem. Only the condition $M/M_B \ll 1$ is important. This makes it possible to distinguish two scales of the collisional relaxation rate: in orientations (ν_i) and in the magnitude ($\nu_i M/M_B$) of the velocity **v** of the resonant particles.

It is to be expected that for $M/M_B \lesssim 1$ an increase in the radiation intensity leads to an insignificant shift of the absorption line center with the linewidth remaining practically unchanged. This is supported by the results of solving the problem of the interaction of radiation with a three-level Λ-system in the strong-collision model,[11] which solves the problem fairly well when $M/M_B \lesssim 1$. For instance, for

$$\kappa_0 \equiv \frac{2|G|^2}{\Gamma \nu_n} \gg 1, \quad \nu_n \ll \Gamma_m, \tag{5.5}$$

and in the event of Doppler broadening ($y \ll 1$), the expression for the absorption probability in the strong-collision model follows from Ref. 11:

$$P_s=\frac{\sqrt{\pi}\,\nu_n y \sqrt{\kappa_0}}{\sqrt{w_n w_l}} \frac{\exp[-\delta^2/4-x_0^2]}{\sqrt{w_l}\exp(\delta x_0)+\sqrt{w_n}\exp(-\delta x_0)} \tag{5.6}$$

(for $\kappa_0 \ll 1$, which is equivalent to P being much lower than $y\nu_n$, the solution given in Ref. 11 coincides, as expected, with the model-free solution (2.16)). An increase in radiation intensity from $\kappa_0 \ll 1$ to $\kappa_0 \gg 1$, which is equivalent to the growth in absorption probability from $P \ll y\nu_n$ to $P \sim y\nu_n$, in the strong-collision model only produces only an insignificant shift in the profile of $\alpha_s = P_s/(P_s)_{\max}$ with practically no change in the linewidth. A comparison of the curves *1* and *2* in Figs. 2 and 3 makes this evident.

To clarify the physical picture of the effect of line narrowing, Fig. 4 gives the distributions of the populations in the absolute value of **v** involving the ground-state hyperfine components n and l in the Doppler limit $y \ll 1$. Only atoms whose absolute value of velocity, $t \equiv v/\bar{v}$, is no lower than $|x_i|$ interact with radiation involving the levels $i=n,l$, i.e., the radiation–atom interaction function $\Psi_i(t)$ [see Eq. (4.9)] resembles a step beginning at $t=|x_i|$:

$$\Psi_i(t)=0, \quad (0 \leqslant t < |x_i|),$$
$$\Psi i(t)=\pi \quad (t \geqslant |x_i|). \tag{5.7}$$

The total absorption probability P_L specified by (4.15) is proportional to the sum (with weight t) of the areas for $t \geqslant |x_i|$ under the curves representing the distribution of populations on the levels $i=n,l$:

$$P_L=P_n+P_l, \quad P_i \propto \int_{|x_i|}^{\infty} t\rho_i(t)\,dt, \quad i=n,l. \tag{5.8}$$

Let us now discuss qualitatively the distribution of populations on the levels n and l (Fig. 4). Owing to optical pumping, particles with velocities $t \geqslant |x_l|$ are "pumped" from the level l to the level n (through the level m), while particles with velocities $t \geqslant |x_n|$ are pumped from n to l. Only particles already on level l can land in the velocity interval $|x_l| \leqslant t \leqslant |x_n|$ on l, and this "landing" is possible only as a result of elastic collisions on the level l, with the rate of arrival equal to $y\nu_n M/M_B$ (we assume that $\nu_l=\nu_n$ and $M/M_B \ll 1$). For low radiation intensity, such that $P_i \ll y\nu_n M/M_B$, deviation from the Maxwellian velocity distribution on the levels n and l is observed; only the integral population changes (the curves *2* in comparison to the curves *3* in Fig. 4). The situation changes dramatically, however, when the absorption probability is high, $P_i \gg y\nu_n M/M_B$: the population $\rho_l(t)$ in the velocity interval $|x_l| \leqslant t \leqslant |x_n|$ is depleted and is has "no time" to be "filled up" by collisions, while the population $\rho_n(t)$ in the same interval grows (curves *1* in Fig. 4).

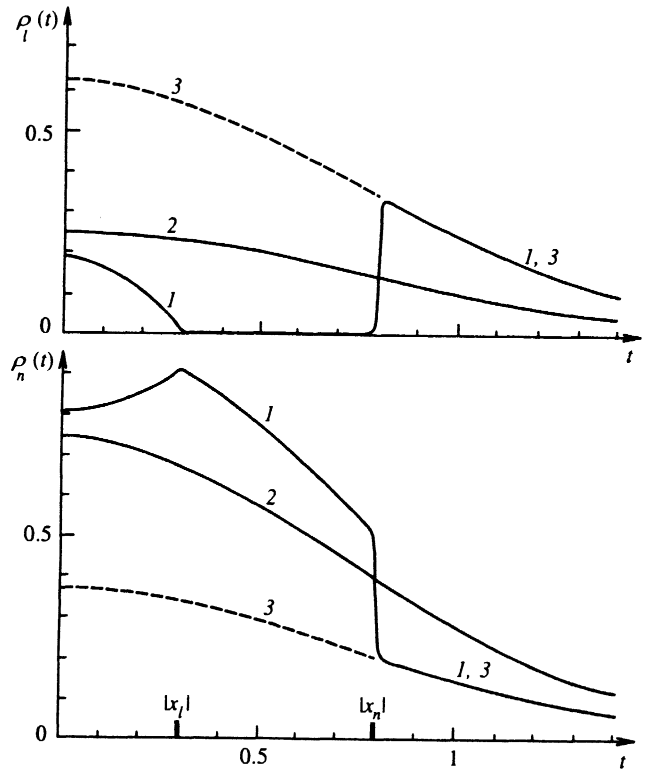

FIG. 4. Populations (in arbitrary units), in the absolute value of velocity, of the ground-state hyperfine levels n and l in the Doppler limit $y \ll 1$ at $w_n = 3/8$ and $w_l = 5/8$. Curves *1* correspond to an elevated radiation intensity and a Lorentz gas (calculations in conditions (4.5) by Eq. (4.14) at $|x_l| = 0.3$ and $|x_n| = 0.8$, which is equivalent to $\delta = 1.1$ and $x_0 = 0.25$ or $\delta = 0.5$ and $x_0 = 0.55$); curves 2 correspond to a low radiation intensity (calculations in conditions (2.12) by Eq. (2.15) at $|x_l| = 0.3$ and $|x_n| = 0.8$; and curves *3* correspond to an equilibrium population in the absence of radiation or when the radiation frequency is tuned to the arithmetic-mean frequency ω_0 of the $m-n$ and $m-l$ transitions ($x_0 = 0$ or, which is the same, $|x_n| = |x_l|$). Equations (2.15) and (4.14) yield the same result at $x_0 = 0$: $\rho_i(v) = N w_i W(v)$.

From comparison of the distributions *1* and 2 in Fig. 4, allowing for the expression (5.8) for P_i, it follows that, all other things being equal, the absorption probability for the distributions *1* is lower than for the distributions *2*. In other words, the absorption line narrows as the distributions *2* are replaced by the distribution *1*, i.e., as the radiation intensity increases.

When the radiation frequency is tuned to the arithmetic-mean frequency ω_0 of the $m-n$ and $m-l$ transitions, i.e., at $|x_0| = 0$, we have $|x_n| = |x_l|$. Here the dip at the level l and the peak at the level n in the distributions *1* (Fig. 4) disappear (the width of the peak and dip, equal to $\| x_n| - |x_l\|$, tends to zero as $|x_0| \to 0$) and the distributions *1* transform into the distributions *3*. The absorption probability P_L specified by (5.8) reaches its maximum, obviously, at $x_0 = 0$. Thus, the center of the absorption line for $P_i \gg y \nu_n M/M_B$ is at point $x_0 = 0$, which is confirmed by Eq. (4.17).

5. CONCLUSION

We have described the effect of absorption-line field narrowing in vapors of light alkali-metal atoms (^{7}Li and ^{23}Na) in an atmosphere of heavy buffer particles of an inert gas (Xe and Kr). Optical pumping to the ground-state hyperfine components is essential for the effect to manifest itself.

In the presence of collisional transitions between the hyperfine-structure components n and l (characterized by the frequency ν_{ln}) the condition for the line-narrowing effect to occur is formulated as follows (cf. Eq. (4.5)):

$$y \nu_i \frac{M}{M_B}, \ \nu_{ln} \ll P_i < \Gamma_m, \ y\nu_i, \quad y \ll 1,$$
$$\nu_i \frac{M}{M_B}, \ \nu_{ln} \ll P_i < \Gamma_m, \ \nu_i, \quad y \gtrsim 1. \tag{6.1}$$

For alkali-metal atoms in an atmosphere of inert gases the transition frequency ν_{ln} is lower by several orders of magnitude than the transport frequency ν_i of elastic collisions,[5] and the effect is present if $M/M_B \ll 1$. But if the buffer gas is not inert, usually $\nu_{ln} > \nu_i$ and the condition (6.1) cannot be met.

In conclusion we estimate the radiation intensity I_0 at which the absorption line begins to narrow. Determining I_0 from the condition that $P_i = y \nu_i M/M_B$, we obtain

$$I_0 \sim \frac{\pi \Gamma \nu_n}{B} \frac{M}{M_B}. \tag{6.2}$$

For ^{7}Li and ^{23}Na atoms the Einstein coefficient B is $1.39 \times 10^{17} w_n$ cm$^2 \cdot$W$^{-1} \cdot$s^{-2} and $1.57 \times 10^{17} w_n$ cm$^2 \cdot$W^{-1} $\cdot$s^{-2}, respectively. Assuming $\nu_n \sim 10^7$ s^{-1} (this corresponds to a buffer gas pressure of roughly 1 torr), $\Gamma \sim 5 \times 10^7$ s^{-1}, and $w_m \sim 1$, we estimate the radiation intensity I_0 at 0.5×10^{-3} W cm^{-2} for the ^{7}Li–Xe mixture and at 2×10^{-3} W cm^{-2} for the ^{23}Na–Xe mixture.

When the buffer gas pressure is much lower than 1 torr, the impact linewidth of absorption of ^{7}Li and ^{23}Na atoms is small compared to the radiative linewidth ($\nu_{mi} \ll \Gamma_m/2$). Here the homogeneous halfwidth in (2.7), $\Gamma \approx \Gamma_m/2$ is pressure-independent and the intensity I_0 specified in (6.2) is proportional to the buffer gas pressure. At pressures much higher than 1 torr the homogeneous halfwidth is proportional to the pressure ($\Gamma \approx \nu_{mi}$), so that I_0 specified in (6.2) becomes a quadratic function of pressure.

The authors are grateful to A. M. Shalagin for fruitful discussions of the results and for a number of valuable suggestions concerning the physics of the effects examined. This work was partially supported by grants from the Russian Fund for Fundamental Research (No. 93-02-03567) and the Soros International Science Foundation (No. RCM000), and was also supported by the Netherlands Organization for Scientific Research and the Universities of Russia Program.

[1] S. G. Rautian, G. I. Smirnov, and A. M. Shalagin, *Nonlinear Resonances in the Spectra of Atoms and Molecules*, Nauka, Novosibirsk (1979).
[2] A. K. Popov, *Introduction into Non-linear Spectroscopy*, Nauka, Novosibirsk (1983).
[3] I. I. Sobelman (Sobel'man), *Atomic Spectra and Radiative Transitions*, Springer, Berlin (1979).
[4] A. D. Streater and J. P. Woerdman, J. Phys. B **22**, 677 (1989).
[5] W. Happer, Rev. Mod. Phys. **44**, 169 (1972).
[6] S. N. Atutov, A. I. Parkhomenko, S. P. Pod"yachev, and A. M. Shalagin, Zh. Éksp. Teor. Fiz. **99**, 378 (1991) [Sov. Phys. JETP **72**, 210 (1991)].
[7] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A.

Stegun, National Bureau of Standards Applied Mathematics Series 55, Washington, D.C. (1979).
[8] E. M. Lifshitz and Pitaevskiĭ, *Physical Kinetics*, Pergamon Press, Oxford (1979).
[9] F. Kh. Gel'mukhanov, L. V. Il'ichov, and A. M. Shalagin, Physica A **137**, 502 (1986).
[10] A. A. Radtsig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions*, Springer, Berlin (1986).
[11] S. N. Atutov, A. I. Parkhomenko, S. P. Pod"yachev, and A. M. Shalagin, J. Phys. B **25**, 2943 (1992).

Translated by Eugene Yankovsky